Thermodynamics: the basics

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Laws of Thermodynamics

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1 The First Law
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The Minus First Law

- AKA *The Equilibrium Principle* (Brown and Uffink 2001)
  - An isolated system in an arbitrary initial state within a finite fixed volume will spontaneously attain a unique state of equilibrium.

- Examples:
  - Thermal Equilibration
  - Equilibration of pressure
  - Chemical reactions

- *Worth emphasizing:* the adverb “quickly” does not appear in the above statement of the Law, and relaxation times vary widely.

- According to Brown and Uffink, it is this law that is the source of temporal asymmetry in thermodynamics.
The Zeroth Law

- We can place objects into thermal contact with each other.
- If $A$ and $B$ are brought into thermal contact, then one of three things will happen as the new system equilibrates:
  1. Heat flows from $A$ to $B$.
  2. Heat flows from $B$ to $A$.
  3. No heat flow.
- The Zeroth Law says that condition (3) is transitive:

  \[ \text{If } A \text{ can be brought into thermal contact with } B \text{ without heat flow, and } B \text{ can be brought into thermal contact with } C \text{ without heat flow, then } A \text{ can be brought into thermal contact with } C \text{ without heat flow.} \]
Thermodynamics: the basics

Zeroth Law and Equitemperature

If A can be brought into thermal contact with B without heat flow, and B can be brought into thermal contact with C without heat flow, then A can be brought into thermal contact with C without heat flow.

This allows us to define an equivalence relation on equilibrium states: If A and B are equilibrium states, these states are equitemperature states iff A and B can be brought into thermal contact with each other with no heat flow.

Note: we don’t yet have a numerical temperature scale.
The First Law

- The work I do on a system in changing its state from \(a\) to \(b\) is
  \[
  W = - \int_{a}^{b} F \cdot dx,
  \]
  where \(F\) is the force opposing my efforts.
  - \(W\) positive = I do work on the system.
  - \(W\) negative = the system does work on me.
- I can also transfer energy to the system as heat.
- The First Law says that, if work \(W\) is done on a system, and heat \(Q\) passes into it, then the internal energy \(U\) of the system changes by an amount
  \[
  \Delta U = Q + W.
  \]
- Differential form:
  \[
  dU = dQ + dW.
  \]
In a washroom in a physics building
The Second Law

- Kelvin (1851):
  
  *It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.*

- Clausius (1854):
  
  *Heat can never pass from a colder body to a warmer body without some other change, connected therewith, occurring at the same time.*

  *Es kann nie Wärme aus einem kälteren Körper übergehen, wenn nicht gleichzeitig eine andere damit zusammenhängende Änderung eintritt.*
QSR processes

- We distinguish between
  - Quasistatic, reversible processes
  - All other processes (dissipative processes)
Carnot’s theorem

- Suppose we have a heat engine that
  1. Extracts an amount of heat $Q_{in}$ from a hot reservoir;
  2. Performs net work $W$ on its surroundings;
  3. Discards heat $Q_{out}$ into a cold reservoir

- Define efficiency:

  $$\eta = \frac{W}{Q_{in}} = \frac{1}{1 - \frac{Q_{out}}{Q_{in}}}$$

- If we assume the 2nd Law as an axiom, it follows that

  Any two heat engines operating in a qsr manner between two heat reservoirs have the same efficiency, which is dependent only on the temperature of the two reservoirs. Moreover, any other heat engine has lower efficiency.
If \( \eta_{AB} \) is the efficiency of a reversible engine operating between reservoirs \( A \), \( B \), define the thermodynamic temperature \( T \) by

\[
\frac{T_B}{T_A} = df 1 - \eta_{AB}.
\]

This defines a temperature scale up to an arbitrary scale factor.
Ideal Gases

- An *ideal gas* satisfies:
  - *Joule’s law.* The internal energy of the gas is a function only of temperature.
  - *Boyle’s law.* At fixed temperature,
    \[ p \propto \frac{1}{V}. \]
Define ideal gas temperature $\theta$ by

$$\theta \propto pV.$$  

This gives us the equation of state, the *ideal gas law*:

$$pV = nR\theta,$$

where $n$ is the ratio of the amount of gas in our sample to a standard reference quantity (1 mole), and $R$ depends only on choice of units (ideal gas constant).
Comparing the two temperature scales

- What is the relation between the thermodynamic temperature $T$ and the ideal gas temperature $\theta$?

- **Strategy:**
  - Consider an ideal gas heat engine running between two heat reservoirs with i.g. temps $\theta_H$ and $\theta_C$.
  - Pick a reversible cycle that’s particularly easy to analyze.
  - Considering this cycle, we can get the efficiency $\eta(\theta_H, \theta_C)$ as a function of the ideal gas temperatures of our reservoirs.
  - Setting
    \[
    \eta(\theta_H, \theta_C) = 1 - \frac{T_C}{T_H}
    \]
    gives us a relation between the two scales.
Carnot cycle: the punchline

- Analysis of the Carnot cycle yields

\[
\frac{Q_{in}}{\theta_H} = \frac{Q_{out}}{\theta_C}.
\]

- or,

\[
\eta(\theta_H, \theta_C) = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{\theta_C}{\theta_H}.
\]

- Compare

\[
\eta = 1 - \frac{T_C}{T_H}
\]

- This gives

\[
\theta \propto T.
\]
Enter entropy

- For a Carnot cycle,
  \[ \oint \frac{\tilde{Q}}{T} = \frac{Q_{in}}{\theta_H} - \frac{Q_{out}}{\theta_C} = 0. \]

- Moreover, this must be true for any qsr cycle.

- It follows that there is a state function \( S \) such that for any qsr process
  \[ \int_a^b \frac{\tilde{Q}}{T} = S_b - S_a, \]

- or,
  \[ dS = \left( \frac{\tilde{Q}}{T} \right)_{qsr}. \]

- This state function is called the thermodynamic entropy.
This gives us another way of stating the Second Law of Thermodynamics. For any cycle,
\[ \oint \frac{\bar{Q}}{T} \leq 0, \]
with equality holding for reversible processes.

In differential form,
\[ \bar{Q} \leq TdS, \]
with equality holding for reversible processes.

For any processes occurring within an adiabatically isolated system,
\[ dS \geq 0. \]
Entropy of an Ideal Gas

Entropy difference between states \( a \) and \( b \) of an ideal gas is

\[
S_b - S_a = nR \log \left( \frac{V_b}{V_a} \right) + C_V \log \left( \frac{T_b}{T_a} \right).
\]
The Third Law

- No finite sequence of cyclic processes can succeed in cooling a body down to absolute zero.
- The entropy of every pure, crystalline substance approaches the same value as the temperature approaches zero.
- This gives us a natural zero-point for entropy.